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DEPARTMENT OF CHEMISTRY

CALVIN COLLEGE

Grand Rapids, Michigan

Investigation of the Electrode Migration and Reaction
Process Occurring in Alkaline-Zinc Batteries

Contract No. AF 33(615)-3292

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Prepared by: T. P. Dirkse

FOREWORD

This report was prepared by Calvin College, Grand Rapids, Michigan, for the AF Aero Propulsion Laboratory at Wright-Patterson Air Force Base, Ohio, on Contract No. AF 33(615)-3292. Mr. J. E. Cooper is task engineer for this project.

The work covered by this report was accomplished under Air Force Contract AF 33(615)-3292, but this report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

TABLE OF CONTENTS

	Page
Foreword	1
Table of Contents	11
Abstract	111
Zinc Corrosion	
Introduction	1
Experimental	2
Results	2
Discussion	3
Program for Next Quarter	5
List of References	6
Captions for Figures	7

ABSTRACT

The corrosion rate of zinc in KOH solutions has been measured under a variety of conditions. Amalgamation and the presence of zincate ions lower this rate of corrosion. The effect of increasing KOH concentration on the rate of corrosion is different for non-amalgamated zinc than for amalgamated zinc. The temperature effect is also different for the two types of zinc electrodes.

INTRODUCTION

One of the problems associated with the use of zinc electrodes in alkaline solutions is the reaction of zinc with the electrolyte to produce hydrogen. This reaction has two disadvantages. It uses up the zinc, i.e., it is a self-discharge reaction. Also, the evolution and buildup of hydrogen is undesirable if the cell is to operate in the sealed condition.

The reaction can be described as a corrosion reaction. Over the years there has been considerable interest in the corrosion of zinc but hardly any work has been published on the corrosion of zinc in alkaline solution.

Snyder and Lander (1) studied the evolution of hydrogen from commercial zinc electrodes containing 2% polyvinylalcohol and encased in a cellulosic separator material. They found that the amount of hydrogen evolved in a given time decreased as the electrolyte changed from 30 to 45% KOH. It decreased with increasing HgO content up to 4%, and it also decreased with decreasing temperature. Furthermore, the presence of zincate in the electrolyte increased the amount of hydrogen evolved.

Ruetschi (2) also studied the corrosion rate of amalgamated zinc in alkaline solutions. His experimental arrangement avoided the use of separators and additives. He used a specified weight of powdered material but no surface area values were given. Consequently, the rate of corrosion per unit surface area cannot be determined from his data. The corrosion of amalgamated zinc was found to increase with increasing temperature. It increased with increasing KOH concentrations, contrary to the results of Snyder and Lander (1). Furthermore, the presence of zincate ions decreased the rate of corrosion except in KOH solutions less than 2 N. Here the zincate ion appeared to have a catalytic effect.

The main discrepancies between the work of Ruetschi and that of Snyder and Lander are (1) the effect of zincate ion and (2) the effect of increasing KOH concentration on the corrosion rate of amalgamated zinc. Some of this difference may be due to the way in which the data were obtained. Snyder and Lander used as the corrosion rate, the steady state achieved after about 30 days. Ruetschi started taking measurements less than 24 hours after the zinc and KOH were brought in contact with each other. Thus, in the work of Snyder and Lander, the electrolyte composition at the time measurements were taken was likely somewhat different from that at the time the corrosion began. Furthermore, in the work of Snyder and Lander the corrosion rate was likely also affected by the polyvinyl alcohol and the separator material.

The present work on the corrosion of zinc in alkaline solutions was undertaken for two reasons: (1) because so little work has been reported on this matter; and (2) to establish basic information on the effect of KOH concentration, amalgamation, zincate ion, and temperature on this process. These values are needed so that one can determine, with such information as a background, the effect of additives and impurities on the corrosion rate of zinc in a battery system.

EXPERIMENTAL

The apparatus consisted of a sealed glass tube about 2.5 x 20 cm. to which a calibrated pipette was attached. The entire assembly, except for the outlet of the pipette was immersed in a liquid constant temperature bath. Two pieces of zinc (99.999%) wire, 12.7 cm. x 0.15 cm. were placed in the electrolyte. Thus the surface area exposed to the electrolyte was 12 cm.²

As hydrogen was evolved, liquid was forced into the pipette. Consequently, the rise in the liquid level in the pipette was a measure of the rate at which hydrogen was evolved. In each run a blank (containing no zinc wire) was included to correct for minor fluctuations due to changes in barometric pressure. Corrections were also made for vapor pressure, etc., and the results were then expressed as micromoles of hydrogen evolved per sq. cm. of electrode area. Measurements were begun within an hour after the apparatus was assembled.

RESULTS

A typical set of data is shown on Figure 1. The slope of these lines served as a measure of the rate of corrosion, i.e., rate of hydrogen evolution. This rate was measured in 20, 30, 35, 40, and 45% KOH and in these same solutions saturated with zinc oxide. Both amalgamated and non-amalgamated zinc electrodes were used and every run was made at two temperatures: 25 and 44° C.

The variation of the rate of corrosion with these differing conditions can be seen on Figures 2-7. Figure 2 shows the effect of temperature in plain KOH solutions while Figure 3 shows the effect for solutions saturated with ZnO. On this and other figures, lines are drawn through most of the data points. However, on such lines minor fluctuations are not necessarily significant. Some duplicate runs were made and, especially at the lower rates, the uncertainty may approach $\pm 20\%$.

In the plain KOH solutions, Fig. 2, temperature seems to have little effect but, surprisingly, the small difference that there is, indicates a lower corrosion rate at the higher temperature. In the zincate solutions, the temperature effect also is small, but here the higher corrosion rate generally occurs at the higher temperature. In any event, the difference in corrosion rates at 25 and 44° is small.

Figure 2 also illustrates the effect of KOH concentration. Increasing KOH concentrations bring about a reduced corrosion rate as was found by Snyder and Lander (1). When the solutions are saturated with zincate, this regularity does not exist but rather the corrosion rate increases up to about 35% KOH and then decreases, Fig. 3.

The effect of zincate ion can be seen by comparing Figures 2 and 3, but it is shown more directly on Figure 4. The solutions designated as KOH + ZnO were all saturated with ZnO so that the zincate concentration increases markedly in going from 20 to 45% KOH. Fig. 5 shows the effect of zincate ion at 44°.

Amalgamation of the zinc electrode also brings about a marked reduction in the corrosion rate, Fig. 6. The amount of amalgamation was not varied so that the effect of increasing quantities of mercury on the corrosion rate cannot be determined from our data.

It is interesting to note that saturating a KOH solution with ZnO has about the same effect in reducing the rate of corrosion as does amalgamation, compare, e.g., Figures 5 and 6. When both factors are present there is a slight decrease over either one alone, Fig. 7. The effect of temperature and KOH concentration on the corrosion of amalgamated zinc is shown on Figure 8.

DISCUSSION

No other reported work was found for the corrosion rate of non-amalgamated zinc in KOH solutions except for a few data reported by Snyder and Lander (1). They found, as we have, that the corrosion rate decreased with increasing KOH concentration.

Amalgamation reduces the corrosion rate. The presence of zincate ion also reduces the rate of hydrogen evolution. This was observed by Ruetschi (2) but not by Snyder and Lander (1).

The temperature interval used in this work was too small to compare with that used in other work (1,2). However, the results for amalgamated zinc do agree with this other reported work so far as comparisons can be made. The behavior of amalgamated zinc is definitely different from that of non-amalgamated zinc. The corrosion of amalgamated zinc appears to reach a maximum in 30 to 35% KOH while the rate for non-amalgamated zinc decreases with increasing KOH concentration. Further, the corrosion rate of non-amalgamated zinc decreases going from 25 to 44° while that of amalgamated zinc increases.

In seeking to formulate a mechanism for this reaction several other factors must also be considered:

- a - the results are not completely reproducible;
- b - amalgamation markedly reduces the corrosion rate;
- c - the presence of zincate ion markedly reduces the corrosion rate.

A possible mechanism involves the following processes:



Reactions (2) and (3) may each involve several steps as in the anodic treatment of zinc.

Combining (1) and (2) the overall reaction is



Combining (1) and (3) gives



For both overall reactions, the driving force, energetically, is favorable and practically the same. The reason the reaction is as slow as it is, arises from the overvoltage for the hydrogen evolution, reaction (1). The initial rate of reaction (4) is

$$\text{rate} = k_4 (a_{\text{H}_2\text{O}})^2 \quad (6)$$

while that for reaction (5) is

$$\text{rate} = k_5 \cdot a_{\text{H}_2\text{O}} \quad (7)$$

A plot of log rate vs. log $a_{\text{H}_2\text{O}}$ should then give a slope of 2 for reaction (6) and a slope of (1) for reaction (7). Making such a plot of the data in ref. (3) gives a slope of 1.6. A similar plot of our data for plain zinc in KOH solutions at 25° gives a slope somewhat larger than 1.5, Fig. 9. This may mean that both reactions (6) and (7) take place.

This mechanism can be further checked against the results we have obtained. Reactions (6) and (7), as has just been shown, do agree with the effect of KOH concentration on the rate of corrosion, and the quantitative agreement also is good. As KOH concentration increases, the activity of the water decreases, resulting in a lower rate for reaction (1). This then is the controlling process.

Amalgamating the electrode raises the hydrogen overvoltage considerably and slows down reaction (1) which again limits the overall corrosion reaction. The value of this overvoltage varies with temperature and KOH concentration (4) and this may partly affect the change of corrosion rate with these conditions. The overvoltage has a minimum value at about 9 M KOH. The corrosion rate appears to have a maximum value at this concentration, Fig. 8.

When ZnO is dissolved in KOH solutions, reaction (8), the activity of the water is lowered



and this should decrease the rate of reaction (1). However, the rate decrease that was observed, e.g. in 20% KOH, was far greater than could be accounted for by this process alone. Consequently, some other or additional influence of zincate ion must be present. Ruetschi (2) suggested that the corrosion rate could also depend on the rate of dissolution of interfacial ZnO or $\text{Zn}(\text{OH})_2$. In KOH solutions saturated with ZnO, the oxide or hydroxide produced by the corrosion reaction cannot dissolve in the electrolyte. Consequently, it remains on the surface of the zinc and protects the zinc underneath from further reaction. The extent to which the zinc is protected depends on the porosity of the corrosion product. This same phenomenon could account for the lack of complete reproducibility. Our solutions were not shaken during the course of a given determination. For the corrosion product to continue to dissolve, it was then necessary for that which had dissolved to be transported away from the zinc surface either by diffusion or convection. Our results then were modified somewhat by the randomness of this material transport.

In conclusion, reactions (1) to (3) serve as a satisfactory mechanism to account for the results that have been observed. With pure zinc the process is controlled by reaction (1). With amalgamated zinc, reaction (1) is the limiting process because of the higher hydrogen overvoltage. When zincate ion is present, reaction (2) or (3) becomes the limiting one.

Still unaccounted for is the fact that the corrosion rate for non-amalgamated zinc is slightly lower at 44° than at 25°. This cannot be attributed to decreasing activity of water or to increasing hydrogen overvoltage as the temperature is raised. Further, one would expect the rate of dissolution of ZnO or Zn(OH)₂ to be greater at the higher temperature. This leaves as a possible explanation the suggestion that the corrosion product at 44° is more dense than that at 25°. This more dense product affords a more complete covering of the zinc at the higher temperature and lowers the corrosion rate. It has been pointed out (5) that below 35 to 40° a Zn(OH)₂ is a stable form while above this temperature ZnO is the stable phase. Gilbert (6) found that the corrosion of zinc in distilled water at 85° produced only ZnO, while at room temperature the product was ZnO + various types of Zn(OH)₂. Furthermore, Zn(OH)₂ is more soluble than ZnO. Thus it is a possibility that the corrosion of non-amalgamated zinc in alkaline solutions at 25° produces a less dense, and more soluble, product than that which is produced at 44°. Consequently, a more protective covering is formed at the higher temperature giving rise to a lower rate of corrosion.

PROGRAM FOR NEXT QUARTER

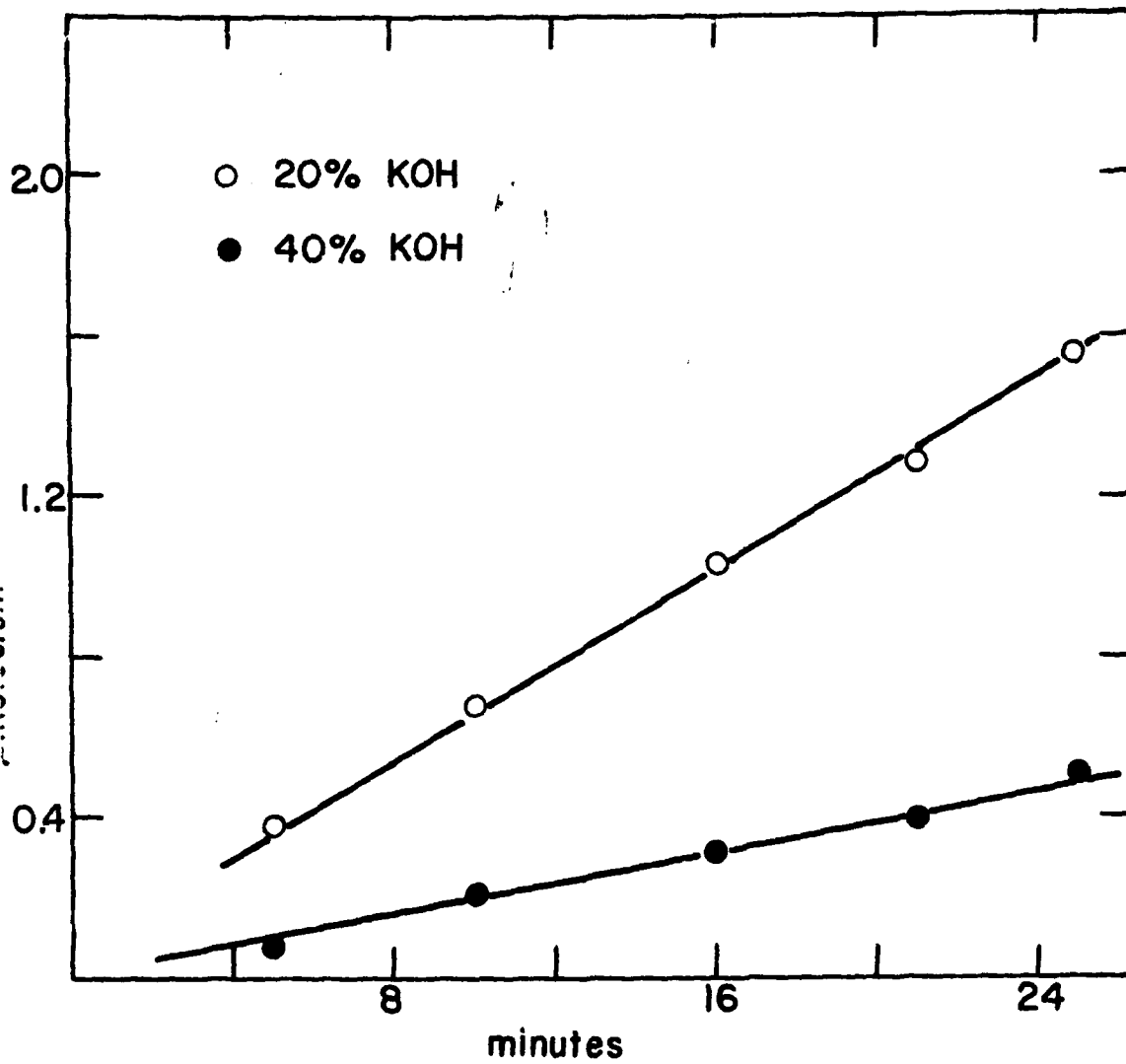
An attempt will be made to get more experimental information about the conditions under which a zinc electrode becomes passive during anodic treatment. Attempts will also be made to study and prepare zinc hydroxide.

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- 4 - Z. A. Iofa, L. Vikomlev, and V. S. Gagotskii, *Zhur. Fiz. Khim.* 35, 1571 (1961).
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- 6 - P. T. Gilbert, *J. Electrochem. Soc.* 99, 16 (1952)

CAPTIONS FOR FIGURES

- Figure 1. Rate of hydrogen evolution from non-amalgamated zinc at 25° C.
- Figure 2. Rate of hydrogen evolution from non-amalgamated zinc as a function of KOH concentration and temperature.
- Figure 3. Effect of dissolved ZnO on the rate of hydrogen evolution from non-amalgamated zinc. All solutions are saturated with ZnO.
- Figure 4. Rate of hydrogen evolution from non-amalgamated zinc at 25°C.
- Figure 5. Rate of hydrogen evolution from non-amalgamated zinc at 44°C.
- Figure 6. Rate of hydrogen evolution at 44°C.
- Figure 7. Rate of hydrogen evolution from amalgamated zinc at 44°C.
- Figure 8. Rate of hydrogen evolution from amalgamated zinc in KOH solutions.
- Figure 9. Log rate vs. log a_{H_2O} plot for hydrogen evolution from zinc in KOH solutions at 25°C.



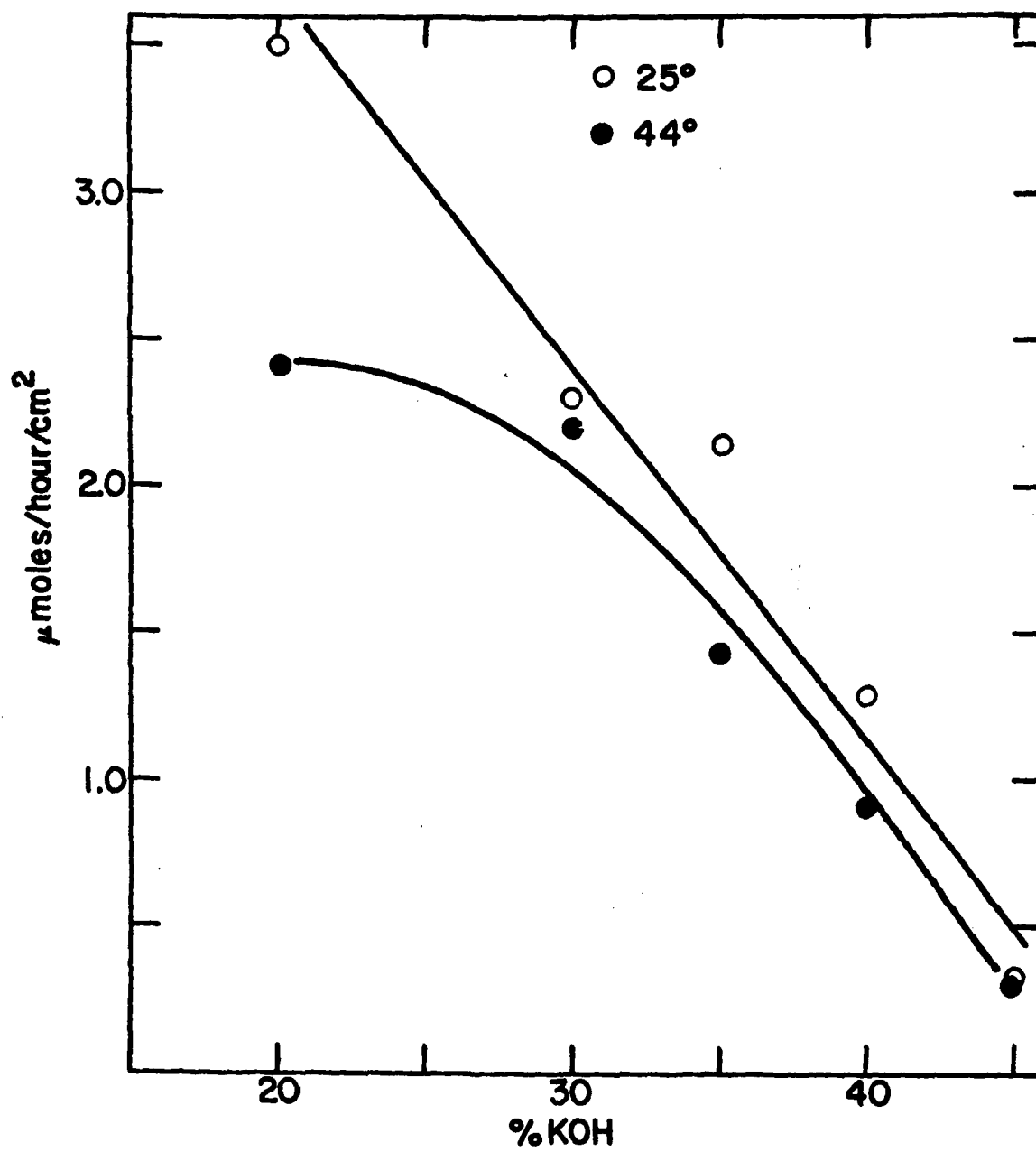


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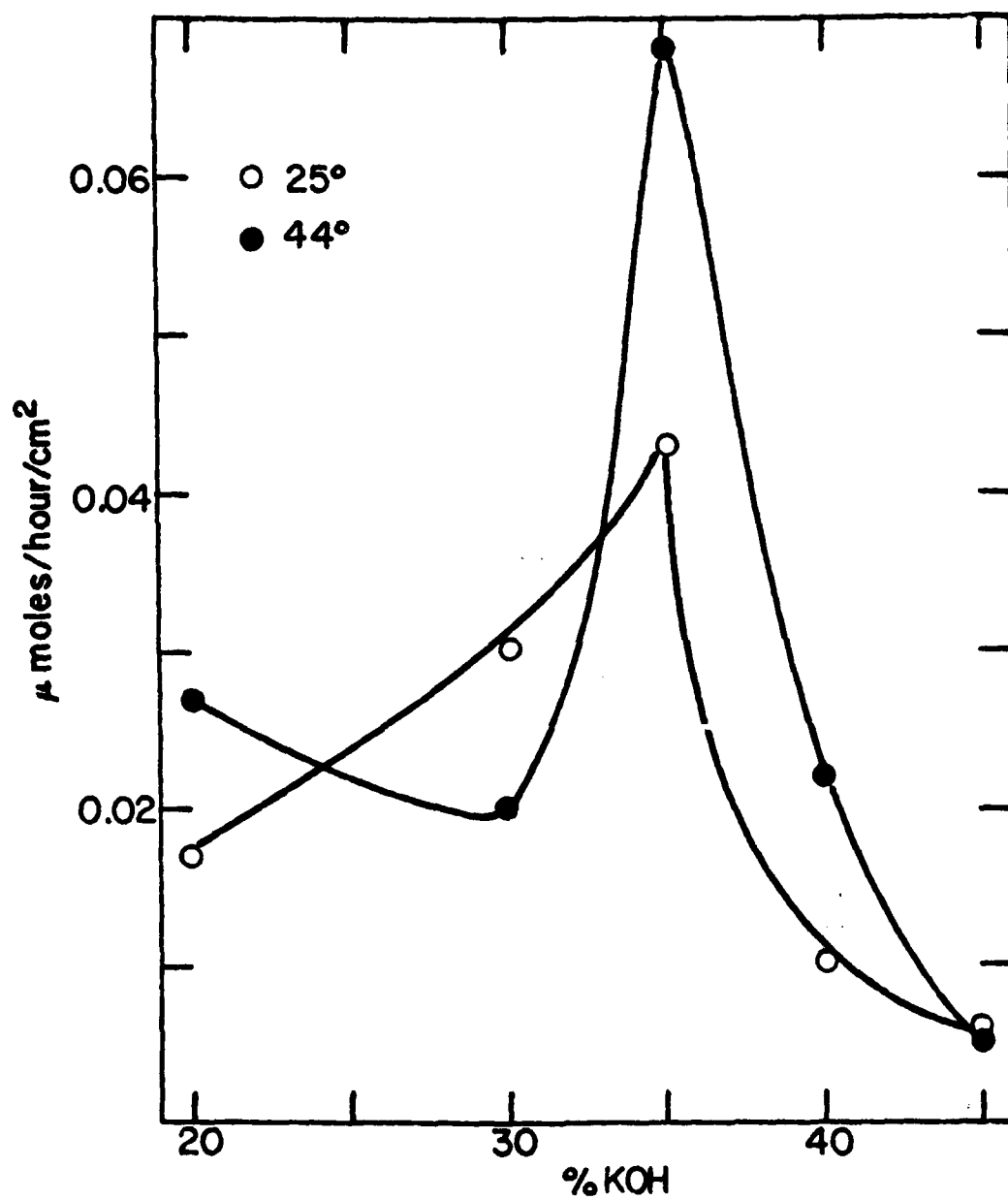


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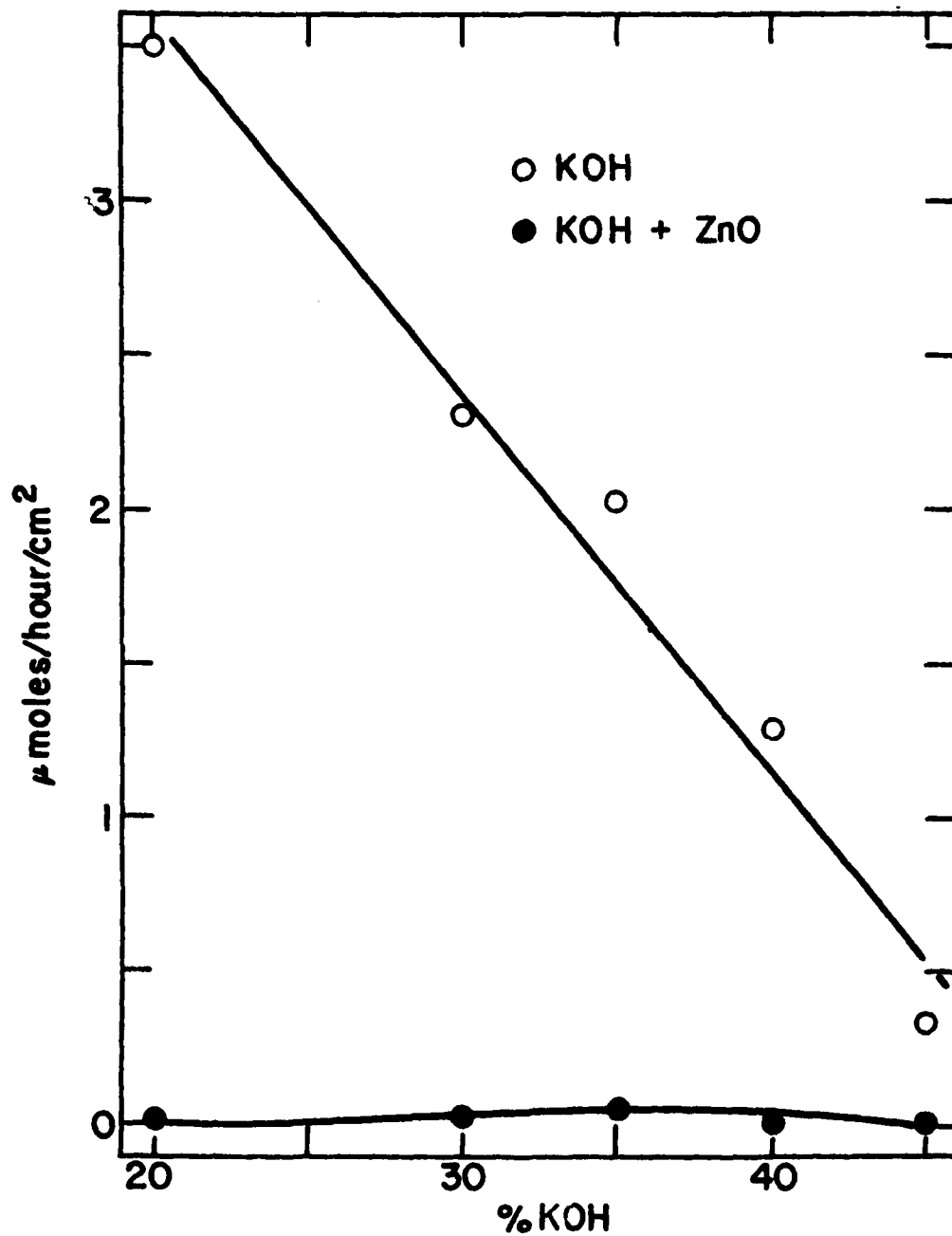


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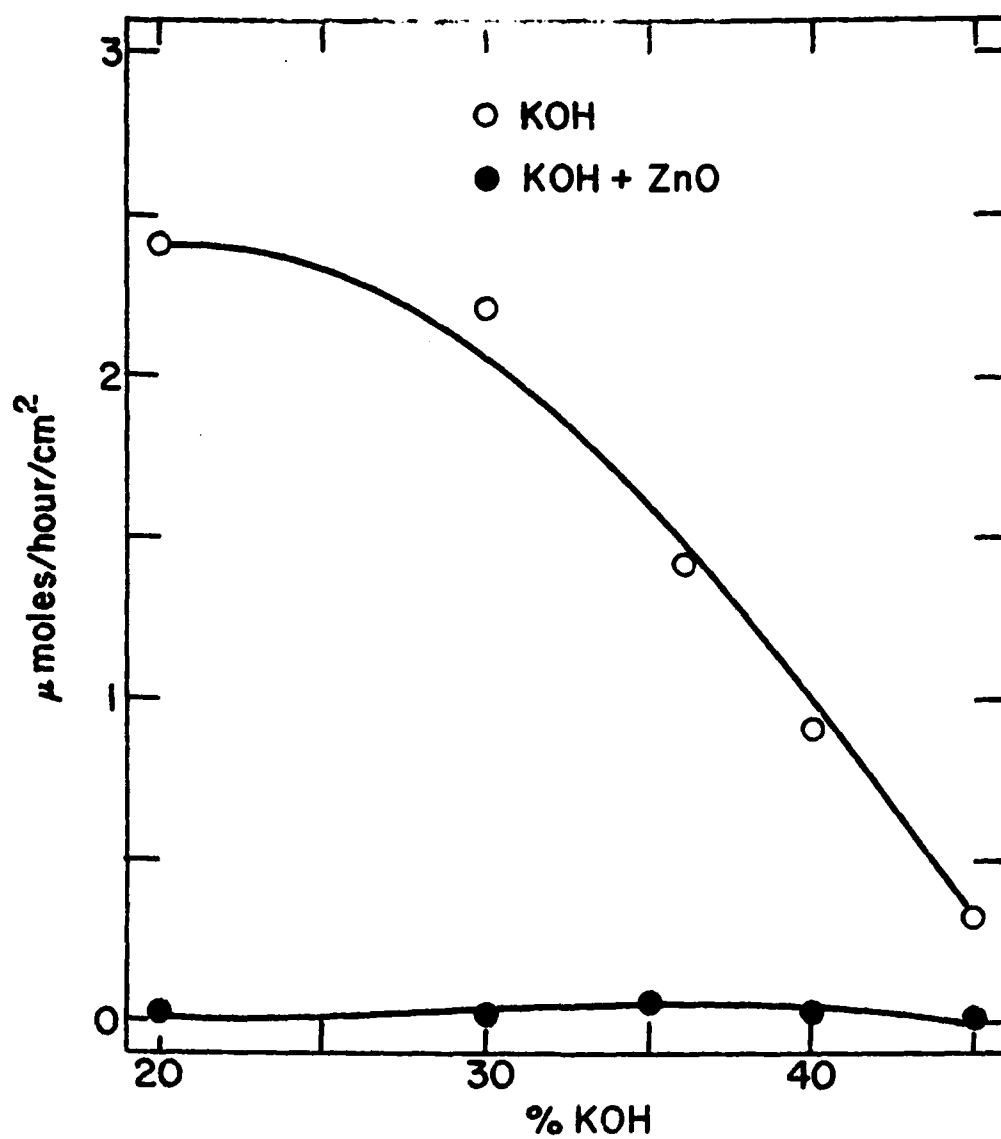


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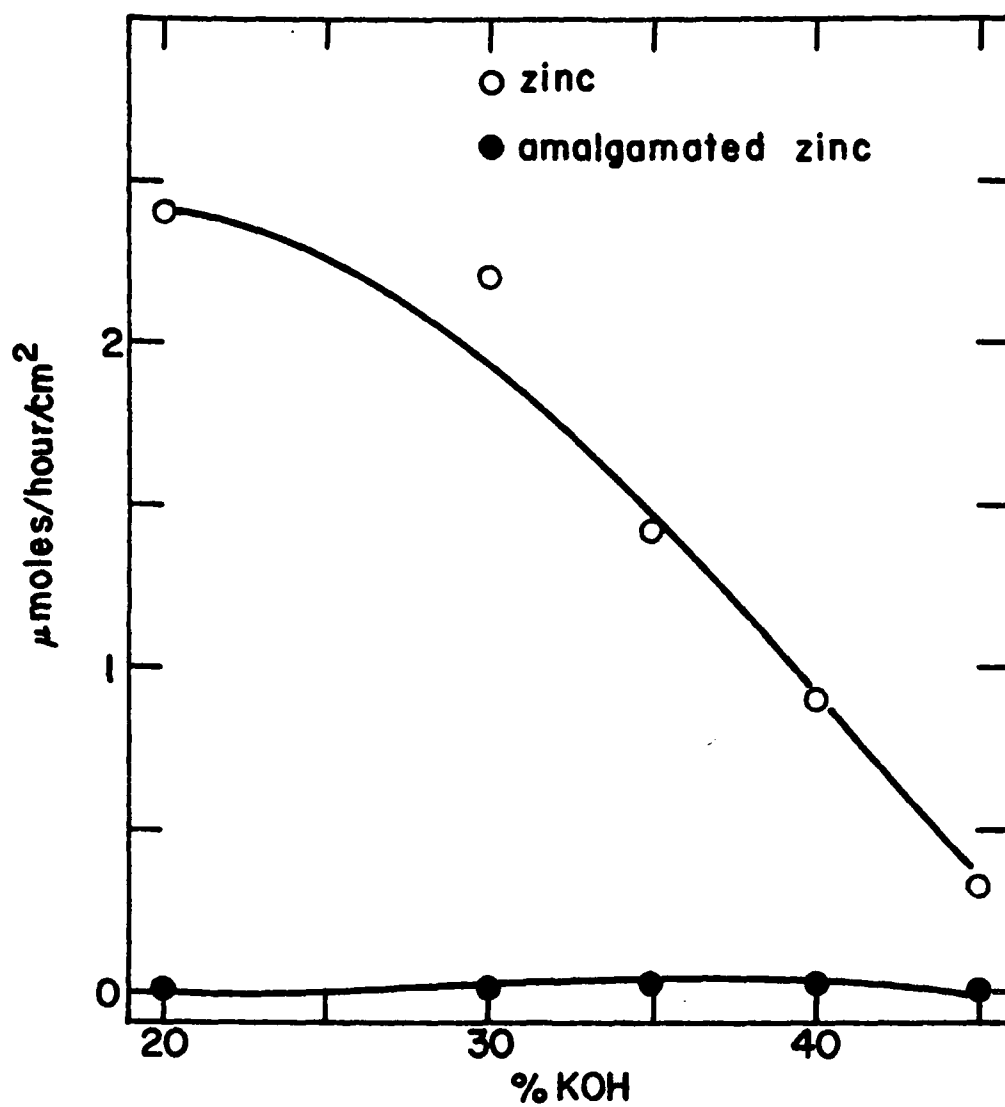


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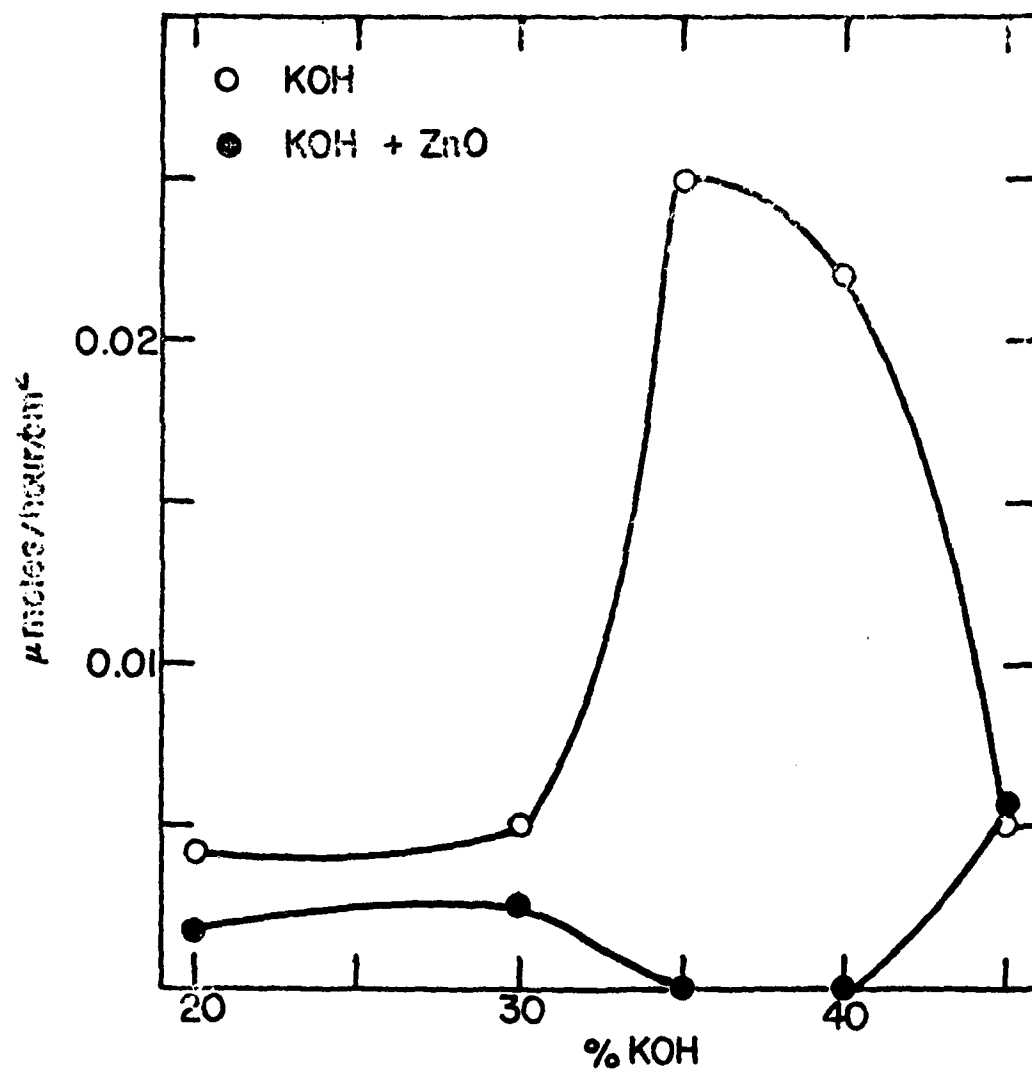


Figure 7

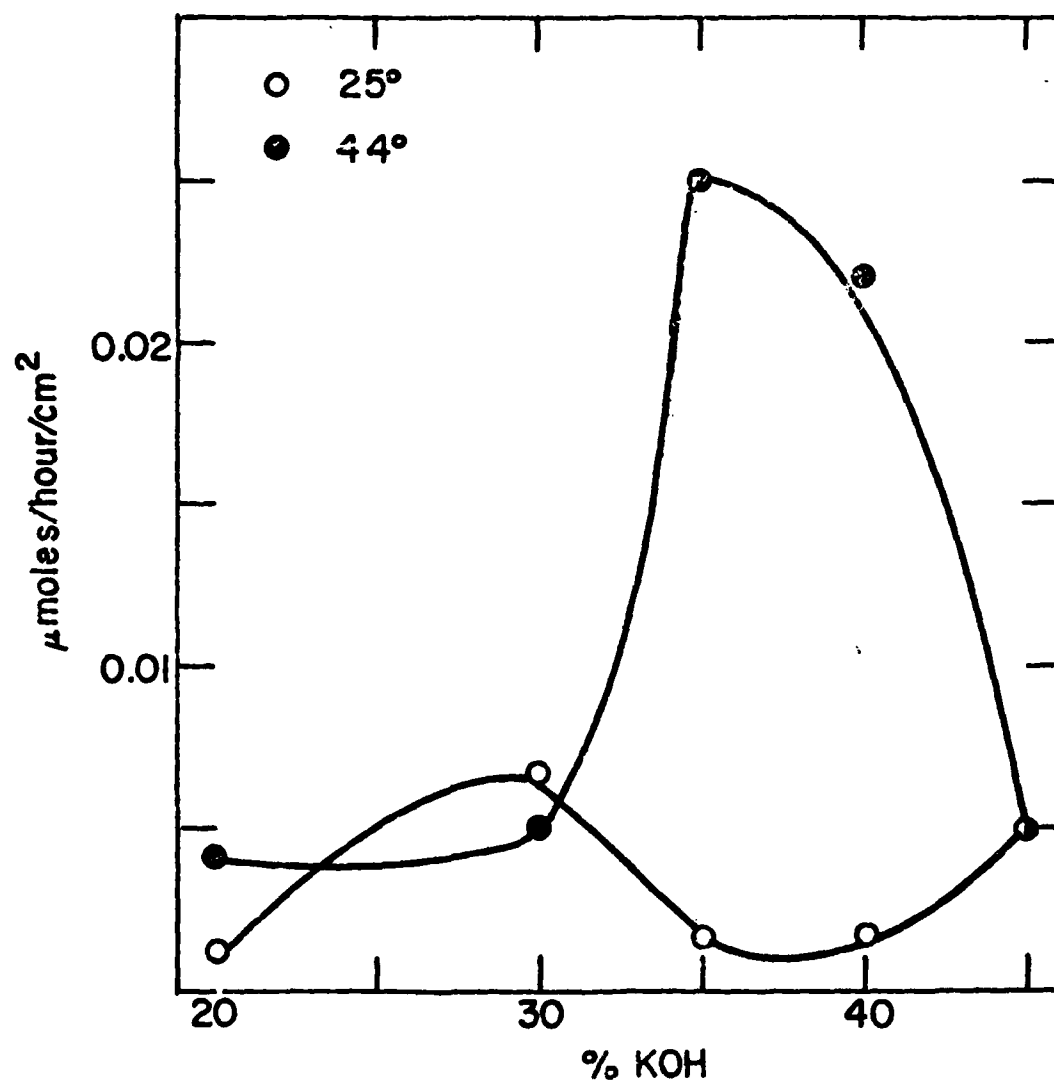


Figure 3

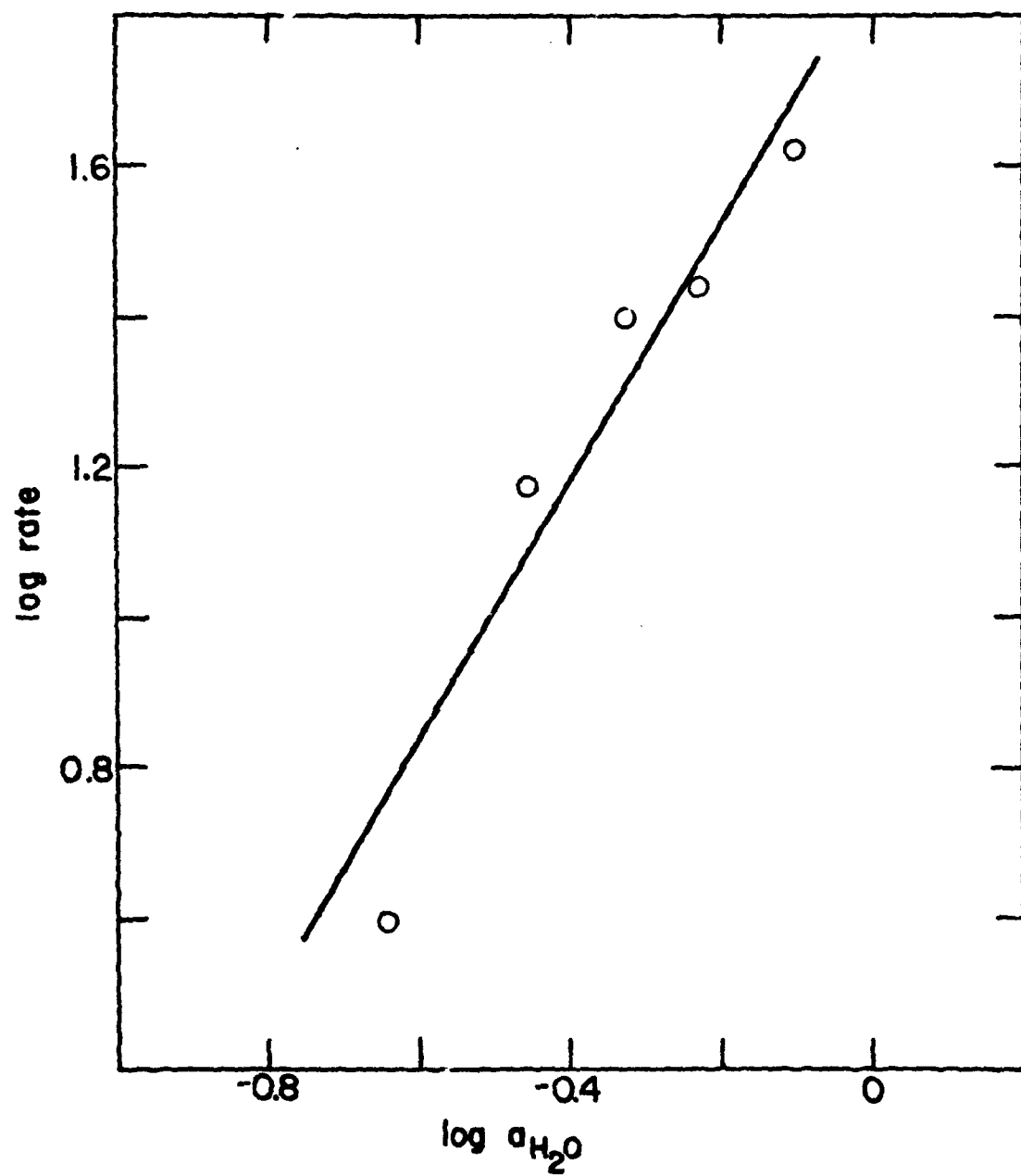


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